

CLAIMS

1. A stabilized composition for use in impregnating catalyst carriers comprising:

- (A) water;
- (B) catalytically active metals being in the form of and comprising:

- (1) at least one component providing at least one metal from Group VIB of the periodic table; and

- (2) at least one component providing at least one metal from Group VIII of the periodic table;

wherein

- (i) said Group VIII metal is provided by a substantially water insoluble component;

- (ii) the molar ratio of said Group VIII metal to Group VIB metal is about 0.05 to about 0.45, provided that the amount of said Group VIII metal is sufficient to promote the catalytic effect of said Group VIB metal;

- (iii) the concentration of said Group VIB metal, expressed as the oxide, is at least about 3 to about 50 weight percent based on the weight of said composition; and

- (C) at least one substantially water-soluble, phosphorous-containing acidic component in an amount sufficient to provide a phosphorous to Group VIB metal molar ratio of about 0.05 to less than about 0.25.

2. A composition according to claim 1 wherein said molar ratio of Group VIII metal to Group VIB metal is about 0.05 to about 0.40.

3. A composition according to claim 2 wherein said molar ratio is about 0.05 to about 0.30.

4. A composition according to claim 2 wherein said molar ratio is about 0.10 to about 0.25.

5. A composition according to claim 1 wherein the concentration of said Group VIB metal is at least about 26 to about 46 weight percent.

6. A composition according to claim 5 wherein the concentration of said Group VIB metal is about 28 to about 42 weight percent.

7. A composition according to claim 1 wherein the concentration of said Group VIB metal is at least about 3 to about 6 weight percent.

8. A composition according to claim 7 wherein the concentration of said Group VIB metal is at least about 3.5 to about 5.5 weight percent.

9. A composition according to claim 1 wherein the concentration of said Group VIB metal is at least about 12 to about 48 weight percent.

10. A composition according to claim 1 wherein said molar ratio of phosphorous to Group VIB metal is about 0.07 to about 0.23.

11. A composition according to claim 10 wherein said molar ratio of phosphorous to Group VIB metal is about 0.08 to about 0.20.

12. A composition according to claim 10 wherein said molar ratio of phosphorous to Group VIB metal is about 0.09 to about 0.18.

13. A composition according to claim 1 wherein said Group VIII component is selected from the group consisting of a nickel carbonate and cobalt carbonate.

14. A composition according to claim 1 further comprising an additional amount of an element from Group VIII in the form of a substantially water-soluble component.

15. A composition according to claim 14 wherein the molar ratio of total Group VIII metal to Group VIB metal is about 0.05 to about 1.0.

16. A composition according to claim 14 wherein the molar ratio of total Group VIII metal to Group VIB metal is about 0.20 to about 0.95.

17. A composition according to claim 14 wherein the molar ratio of total Group VIII metal to Group VIB metal is about 0.30 to about 0.9.

18. A composition according to claim 2 wherein said component of a Group VIII metal is nickel carbonate.

19. A composition according to claim 14 wherein said substantially water-soluble component is nickel nitrate.

20. A composition according to claim 1 wherein said acidic component is orthophosphoric acid.

21. A composition according to any of claims 1 through 7 wherein said Group VIB metal is selected from molybdenum or tungsten.

22. A composition according to claim 21 wherein said Group VIB metal is molybdenum.

23. A composition according to claim 21 wherein said Group VIB component is MoO_3 .

24. A composition for use in preparing a catalytically active solid, said composition comprising:

(A) water in a quantity sufficient to provide a shaped foraminous catalyst mixture;

(B) catalytically active metals useful in chemically refining hydrocarbons, said metals in the form of at least one component providing at least one metal from Group VIB of the periodic table and at least one component providing at least one metal from Group VIII of the periodic table, wherein the molar ratio of said Group VIII metal to Group VIB metal is about 0.05 to about 0.45, and wherein said Group VIII metal component is provided by a substantially water insoluble component; and

(C) at least one substantially water-soluble phosphorous-containing acidic component in an amount sufficient to provide a phosphorous to Group VIB molar ratio of about 0.05 to about 0.25; and

(D) at least one uncalcined foraminous catalyst carrier.

25. A composition according to claim 24 further comprising up to about 5 wt.% of an aqueous nitric acid component.

26. A composition according to claim 24 wherein said Group VIII component is selected from the group consisting of a nickel carbonate and a cobalt carbonate.

27. A composition according to claim 24 further comprising an additional amount of an element from Group VIII in the form of a substantially water soluble component.

28. A composition according to claim 27 wherein the molar ratio of total Group VIII metal to Group VIB metal is about 0.05 to about 1.0.

29. A composition according to claim 28 wherein the molar ratio of total Group VIII metal to Group VIB metal is about 0.20 to about 0.95.

30. A composition according to claim 28 wherein the molar ratio of total Group VIII metal to Group VIB metal is about 0.30 to about 0.9.

31. A composition according to claim 27 wherein said Group VIII component is a nickel nitrate.

32. A composition according to claim 24 wherein said phosphorous-containing acidic component is orthophosphoric acid.

33. A composition according to any one of claims 24 or 32 wherein said acidic component is present in an amount to provide a phosphorous to Group VIB molar ratio of about 0.05 to about 0.25.

34. A composition according to claim 33 wherein said molar ratio of phosphorous to Group VIB metal is about 0.07 to about 0.23.

35. A composition according to claim 34 wherein said molar ratio of phosphorous to Group VIB metal is about 0.08 to about 0.20.

36. A composition according to claim 34 wherein said molar ratio of phosphorous to Group VIB metal is about 0.09 to about 0.18.

37. A composition according to claim 26 wherein said Group VIII component is nickel carbonate.

38. A composition according to any one of claims 24 through 32 and 37 wherein said Group VI metal is selected from molybdenum or tungsten.

39. A composition according to claim 38 wherein said Group VI metal is molybdenum.

40. A composition according to claim 24 wherein said molar ratio of Group VIII metal to Group VIB metal is about 0.05 to about 0.40.

41. A composition according to claim 40 wherein said molar ratio is about 0.05 to about 0.30.

42. A composition according to claim 40 wherein said molar ratio is about 0.10 to about 0.25.

43. A composition according to claim 24 wherein the concentration of said Group VIB metal is at least about 3 to about 50 weight percent.

44. A composition according to claim 24 wherein the concentration of said Group VIB metal is about 26 to about 46 weight percent.

45. A composition according to claim 44 wherein the concentration of said Group VIB metal is at least about 28 to about 42 weight percent.

46. A composition according to claim 24 wherein the concentration of said Group VIB metal is about 3 to about 6 weight percent.

47. A composition according to claim 46 wherein the concentration of said Group VIB metal is at least about 3.5 to about 5.5 weight percent.

48. A composition according to claim 43 wherein the concentration of said Group VIB metal is at least about 12 to about 48 weight percent.

49. A composition according to any one of claims 24 through 32 and 37 wherein said foraminous catalyst carrier is at least one member selected from the group consisting of silica, silica-gel, silica-alumina, alumina, titania, titania-alumina, zirconia, boria, terrana, kaolin, magnesium silicate, magnesium carbonate, magnesium oxide, activated carbon, aluminum oxide, precipitated aluminum oxide, activated alumina, bauxite, kieselguhr, pumice, natural clays, synthetic clays, cationic clays or anionic clays such as saponite, bentonite, kaolin, sepiolite or hydrotalcite, and mixtures thereof.

50. A composition according to any one of claims 24 through 32 and 37 wherein said foraminous catalyst carrier is selected

from the group consisting of alumina, silica, silica-alumina, titania, titania-alumina, zirconia, natural clay, synthetic clay, and mixtures thereof.

51. A composition according to claim 50 wherein said foraminous catalyst carrier is at least one member selected from the group consisting of silica, silica-alumina, alumina, natural clays, synthetic clays, and mixtures thereof.

52. A composition according to claim 51 wherein said foraminous catalyst carrier is alumina.

53. A method of preparing stabilized aqueous compositions for use in impregnating catalyst carriers to produce catalyst precursors and catalysts, comprising adding to a suitable quantity of water:

(A) at least one substantially water insoluble Group VIII metal component; and

(B) at least one substantially water-soluble, phosphorous-containing acidic component in an amount insufficient to cause dissolution of said Group VIII metal component so as to produce a slurry, and combining said slurry with:

(C) at least one Group VIB metal component; and

(D) mixing the combination of (A), (B) and (C) and heating the mixture, for a time and to a temperature sufficient for (A), (B) and (C) to form a solution; and

(E) adding an additional amount of water, if required, to obtain solution concentrations of said at least one Group VIII metal, said at least one Group VIB metal and phosphorous useful for impregnating said carriers; wherein Group VIB and Group VIII refer to Groups of the periodic table of the elements.

54. The method according to claim 53 wherein the amount of said phosphorous-containing acidic component provides a phosphorous to Group VIB metal molar ratio of about 0.05 to less than about 0.25.

55. A composition according to claim 54 wherein said molar ratio of phosphorous to Group VIB metal is about 0.07 to about 0.23.

56. A composition according to claim 55 wherein said molar ratio of phosphorous to Group VIB metal is about 0.08 to about 0.20.

57. A composition according to claim 55 wherein said molar ratio of phosphorous to Group VIB metal is about 0.09 to about 0.18.

58. The method according to claim 53 wherein said molar ratio of Group VIII metal to Group VIB metal is about 0.05 to about 0.45.

59. The method according to claim 58 wherein said molar ratio is about 0.05 to about 0.40.

60. The method according to claim 59 wherein said molar ratio of Group VIII metal to Group VIB metal is about 0.05 to about 0.30.

61. The method according to claim 60 wherein said molar ratio is about 0.10 to about 0.25.

62. The method according to claim 53 wherein the concentration of said Group VIB metal is at least about 3 to about 50 weight percent.

63. The method according to claim 53 wherein the concentration of said Group VIB metal is about 26 to about 46 weight percent.

64. The method according to claim 63 wherein the concentration of said Group VIB metal is about 28 to about 42 weight percent.

65. The method according to claim 53 wherein the concentration of said Group VIB metal is about 3 to about 6 weight percent.

66. The method according to claim 65 wherein the concentration of said Group VIB metal is about 3.5 to about 5.5 weight percent.

67. The method according to claim 62 wherein the concentration of said Group VIB metal is about 12 to about 48 weight percent.

68. The method according to claim 53 wherein said Group VIII metal component is selected from the group consisting of nickel carbonate and cobalt carbonate.

69. The method according to claim 68 wherein said Group VIII metal component is nickel carbonate.

70. The method according to claim 53 further comprising adding an element from Group VIII in the form of a substantially water-soluble component.

71. The method according to claim 70 wherein the molar ratio of total Group VIII metal to Group VIB metal is about 0.05 to about 1.0.

72. The method according to claim 70 wherein the molar ratio of total Group VIII metal to Group VIB metal is about 0.20 to about 0.95.

73. The method according to claim 70 wherein the molar ratio of total Group VIII metal to Group VIB metal is about 0.30 to about 0.9.

74. The method according to claim 70 wherein said Group VIII metal component is nickel nitrate.

75. The method according to any of claims 53 through 57 wherein said acidic component is orthophosphoric acid.

76. The method according to any of claims 53 and 62 through 67 wherein said Group VIB metal is selected from molybdenum or tungsten.

77. The method according to claim 76 wherein said acidic component is orthophosphoric acid.

78. The method according to claim 76 wherein said Group VIB metal is molybdenum.

79. The method according to claim 78 wherein said component providing at least one Group VI metal is molybdenum trioxide.

80. A catalyst prepared by impregnation of a catalyst carrier with a stabilized aqueous composition according to any one of claims 1 through 20 and 24 through 32 and including the step

of separating the volatile portion of said solution from the impregnated uncalcined carrier to obtain a dried catalyst having a desired moisture content.

81. The catalyst according to claim 80 wherein said carrier is selected from the group consisting of alumina, silica, silica-alumina, natural clay, synthetic clay and mixtures thereof.

82. The catalyst according to claim 81 wherein said carrier is alumina.

83. The catalyst according to claim 80 and further including the step of forming or shaping the impregnated catalyst carrier.

84. The catalyst according to any one of claims 80 to 83 and further including the step of calcining the dried catalyst.

85. A catalyst useful in hydroprocessing a petroleum feed, said catalyst comprising at least one catalytically active metal from Group VIB of the periodic table, at least one catalytically active metal from Group VIII of the periodic table, and phosphorous, wherein said metals and phosphorous are carried on a foraminous carrier, wherein the pore mode is about 40 to about 90Å, wherein the loss in weight on ignition at 1000°F to 1200°F of said catalyst is less than about 5 wt.% based on the weight of the catalyst, and wherein the ASI ratio is greater than about 0.75 to about 2.0.

86. A catalyst useful in hydrodesulfurization, hydrodenitrification and hydrodemetallation of heavy hydrocarbons, said catalyst comprising at least one catalytically active metal from Group VIB of the periodic

table, at least one catalytically active metal from Group VIII of the periodic table, and phosphorous, wherein said metals and phosphorous are carried on a foraminous carrier, wherein the pore mode is about 40 to about 90Å, wherein the loss in weight on ignition at 1000°F to 1200°F of said catalyst is less than about 5 wt.% based on the weight of the catalyst and wherein the ASI ratio is greater than about 0.75 to about 2.0.

87. A catalyst characterized by its ability to hydrotreat a charge hydrocarbon feed containing components boiling above 1000 °F, and sediment-formers, sulfur compounds, metals, asphaltenes, carbon residue, and nitrogen compounds, said catalyst comprising at least one catalytically active metal from Group VIB of the periodic table, at least one catalytically active metal from Group VIII of the periodic table, and phosphorous, wherein said metals and phosphorous are carried on a foraminous carrier, wherein the pore mode is about 40 to about 90Å wherein the loss in weight on ignition at 1000°F to 1200°F of said catalyst is less than about 5 wt.% based on the weight of the catalyst and wherein the ASI ratio is greater than about 0.75 to about 2.0.

88. The catalyst as in any one of claims 85, 86 and 87 wherein said catalyst has been pre-impregnated, shaped, dried and calcined.

89. A process for the hydrodemetallation, hydrodesulfurization, and hydrocracking of a hydrocarbon feedstock, said process comprising contacting said feedstock in at least one reactor with hydrogen under hydrocracking conditions with a catalyst comprising at least one catalytically active metal from Group VIB of the periodic table, at least one catalytically active metal from Group VIII of the periodic table, and phosphorous, wherein said metals

and phosphorous are carried on a foraminous carrier, wherein the loss in weight on ignition at 1000°F to 1200°F of said catalyst is less than about 5 wt.% based on the weight of the catalyst, and wherein the pore mode is about 40 to about 90Å and wherein the ASI ratio is greater than about 0.75 to about 2.0.

90. The process of claim 89 conducted in at least one ebullated reactor bed.

91. The process of claim 89 conducted in at least one fixed bed reactor.

92. A process for hydrotreating a charge hydrocarbon feed containing components boiling above 1000° F, and sulfur, metals, asphaltenes, and carbon residue or sediment precursors, which comprises:

(a) contacting said charge hydrocarbon feed with hydrogen and a catalyst at isothermal hydrotreating conditions, said catalyst comprising at least one catalytically active metal from Group VIB of the periodic table, at least one catalytically active metal from Group VIII of the periodic table, and phosphorous, wherein said metals and phosphorous are carried on a foraminous carrier, wherein the pore mode is about 40 to about 90Å, wherein the loss in weight on ignition at 1000°F to 1200°F of said catalyst is less than about 5 wt.% based on the weight of the catalyst and wherein the ASI ratio is greater than about 0.75 to about 2.0, thereby forming hydrotreated product containing decreased content of components boiling above 1000°F and decreased sulfur, metals, and decreased carbon residue or sediment; and

(b) recovering said hydrotreated product.

93. A process as claimed in claim 92 wherein said contacting is carried out in at least one ebullated bed reactor.

94. A process as claimed in claim 92 wherein said contacting is carried out in at least one fixed bed reactor.

95. A process for hydroconversion of a charge hydrocarbon feed of boiling point greater than 1000° F to form product having a boiling point less than 1000°F which comprises:

(a) contacting said charge hydrocarbon feed with hydrogen and a catalyst at isothermal hydrotreating conditions, said catalyst comprising at least one catalytically active metal from Group VIB of the periodic table, at least one catalytically active metal from Group VIII of the periodic table, and phosphorous, wherein said metals and phosphorous are carried on a foraminous carrier, wherein the pore mode is about 40 to about 90Å, wherein the loss in weight on ignition at 1000°F to 1200°F of said catalyst is less than about 5 wt.% based on the weight of the catalyst and wherein the ASI ratio is greater than about 0.75 to about 2.0, thereby forming hydrotreated product containing increased content of product having a boiling point less than 1000°F; and

(b) recovering said hydrotreated product.

96. A process as claimed in claim 95 wherein said contacting is carried out in at least one ebullated bed reactor.

97. A process as claimed in claim 95 wherein said contacting is carried out in at least one fixed bed reactor.

98. A hydrocarbon conversion process comprising contacting a hydrocarbon oil with a particulate catalyst under conditions of elevated temperature above 600° F and pressure above 500 p.s.i.g. and with hydrogen, said catalyst comprising at least

one catalytically active metal from Group VIB of the periodic table, at least one catalytically active metal from Group VIII of the periodic table, and phosphorous, wherein said metals and phosphorous are carried on a foraminous carrier, wherein the pore mode is about 40 to about 90Å, wherein the loss in weight on ignition at 1000°F to 1200°F of said catalyst is less than about 5 wt.% based on the weight of the catalyst and wherein the ASI ratio is greater than about 0.75 to about 2.0.

99. A process as claimed in claim 98 wherein said contacting is carried out in at least one ebullated bed reactor.

100. A process as claimed in claim 98 wherein said contacting is carried out in at least one fixed bed reactor.